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Orientational diffusion of the toluene-d_3 methyl group in solutions and polymer matrices

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Abstract—IR spectra of solutions of selectively deuterated toluene $C_6H_5CD_3$ in the region of the asymmetric stretching vibrations of the CD_3 group are studied. Pentane, non-deuterated toluene, dibutyl phthalate, acetone and polymers: polybutadiene (PBD), polypropylene (PP) and polymethyl methacrylate (PMMA) are used as solvents. In order to determine activation enthalpy ΔH^* and entropy ΔS^* of the orientational diffusion of the CD_3 group the temperature dependencies of the absorption band widths δ of the asymmetric vibrations of this group are studied. An original method of estimating the errors in determining the values ΔH^* and ΔS^* within Rakov's approach is propsed and checked. The values obtained for ΔH^* do not exceed 1 kcal mol^{-1}. No correlation of ΔH^* with either the dielectric permittivity or the viscosity of the medium was observed. The glass transition in dibutyl phthalate and PBD, as well as relaxation transitions in PP and PMMA, do not affect the dependence $\delta = f(T)$.

INTRODUCTION

NOTWITHSTANDING the progress in studying vibrational and orientational dynamics of molecules in condensed phase, little attention is paid to studying the effect of medium on these processes. As a rule, the study of the solvent effect is restricted to comparison of data obtained for a pure liquid and a solution in an inert solvent [1–5]. Only a few papers in which the molecular dynamics of one compound are studied in a series of solvents are known [6–9], and most of them are concerned with studying the rotation diffusion of radicals by means of ESR [10]. The influence of medium on the orientation diffusion of small molecular fragments (OH–, CH_3–, etc.) is practically not studied. It is well known that the rapid reorientation of small groups considerably contributes to the broadening of the vibrational bands: therefore methods of vibrational spectroscopy are most suitable for studying these systems. In this paper we use IR spectroscopy in order to determine the parameters of orientational diffusion of the toluene-d_3 methyl group. Selective deuteration enables one to study the region of stretching vibrations of the CD_3 group (2400–2100 cm^{-1}) in which most of the solvents are transparent. The rotation of the toluene methyl group in the gaseous phase is nearly free (the barrier of ~10 cal/mol) [11, 12], and in condensed phase the barrier of reorientation of the group will be mainly determined by the intermolecular interactions.

It should be noted that glass-forming low-molecular liquids and polymers may be used as solvents (or matrices). The mobility of polymer chains and lateral groups is different for various temperature ranges, the changes in the mobility being accompanied by relaxation transitions. The relaxation transitions are investigated by different experimental methods, and the information about the process occurring at such transitions is important. Thus, the influence of the relaxation process in solvent on the barriers of orientational diffusion is of particular interest. Therefore, apart from traditional solvents, glass forming low molecular liquids and polymers were used.

Activation energies for orientational diffusion were determined according to RAKOV's method [13] which we modified in Ref. [14]. We pay a lot of attention to analyzing the accuracy of the determination of activation barriers using IR spectra.

EXPERIMENTAL

Selectively deuterated toluene $C_6H_5CD_3$ (I) was produced by the firm IZOTOP (St Petersburg). The purity of the product was not lower than 99.5%. The purity was confirmed by mass